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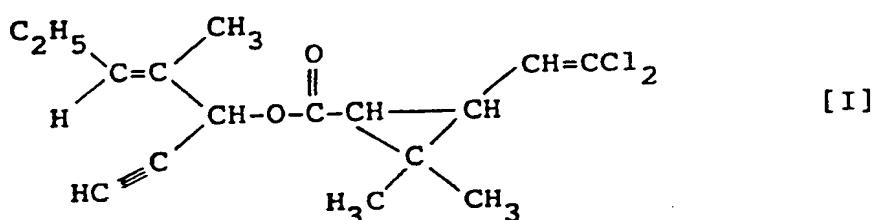
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(58) Field of search

Online databases: CAS ONLINE

(54) Method for controlling insects and/or acarines by vaporising a pyrethroid in the absence of heating

(57) A method for controlling insects and/or acarines comprises vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethylidene)-2,2-dimethylcyclopropanecarboxylate having the formula,



without heating it, i.e. at a temperature in the range 0-30°C.

In contrast with conventional methods, the method of the present invention is useful for controlling insects and/or acarines not only in a narrow space but also in a wider space, such as a room, storage chamber, closet, warehouse, vehicle, ship, airplane, store, cattle shed, stable, drainage trench or sewer for a long period of time.

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METHOD FOR CONTROLLING INSECTS AND/OR ACARINES

1 The present invention relates to a method for controlling insects and/or acarines which comprises vaporizing an active ingredient without heating the same.

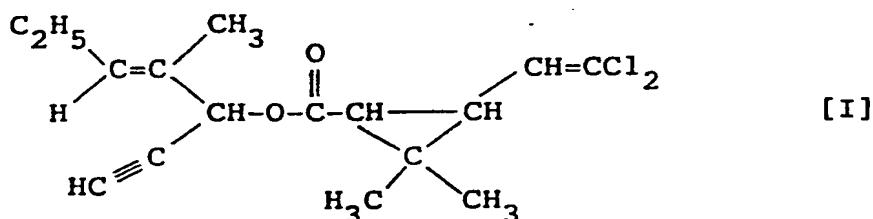
Although various insecticidal and/or acaricidal agents are known today, organophosphorus insecticides such as dichlorvos ($(\text{CH}_3\text{O})_2\text{PO}\cdot\text{OCH}=\text{CCl}_2$) may be an isolated instance for the agents suited for a method for controlling insects and/or acarines comprising vaporizing an active ingredient without actually heating. As a sole instance for such a method with a pyrethroid compound, an insecticide of low toxicity, there has been reduced to practice a method comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl chrysanthemate for controlling pests injurious to clothing.

15 When used in a relatively narrow space such as a chest of drawers, a drawer, etc., 1-ethynyl-2-methyl-2-pentenyl chrysanthemate is effective in controlling pests injurious to clothing. However, unless used in a considerably large amount, this agent is not necessarily effective in controlling pests in a wide space such as room, storage chamber, closet, ware-house, vehicle, ship, airplane, store, cattle shed, stable, drainage trench, sewer, etc. Also for duration of the activity for a long period of time, the agent should be used in a large amount.

25 Vaporization of an active ingredient by heating

1 is sometimes effective in enhancing the initial efficacy.
But, saving in energy is required for protecting the earth
environment. If an active ingredient can be vaporized
without heating, it will become possible to save precious
5 energy. Moreover, there can be prevented dangers of burning
and fire due to a heating element or heat generator for
vaporizing the active ingredient.

According to the present invention, there is
provided a method for controlling insects and/or acarines
10 comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl
3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
(hereinafter Compound I) having the formula,



without heating the same.

The present inventors earnestly investigated a
15 method for effectively controlling insects and/or acarines
comprising vaporizing an active ingredient without
heating, and consequently found that out of numerous
well-known insecticidal and acaricidal agents, Compound I
is the most suitable for the object of the present
20 invention, whereby the present invention was accomplished.

It has been disclosed in JP-B-55-42045 that

1 Compound I has an insecticidal and acaricidal activity.
The present inventors, however, found that mere
vaporization of said compound without heating exhibits a
high initial activity against insects and/or acarines and
5 that the activity lasts for a long period of time, whereby
the present inventors were led to the present invention.

The term "without heating" used herein means at
an ordinary temperature (without heating or cooling),
namely, at a temperature not higher than 30°C but higher
10 than about 0°C.

The method of the present invention is effective
against various insect pests and acarine pests. It is
markedly effective against hygienic pests, wood pests,
food stuff pests, household nuisance pests, etc.
15 Particularly, it is most effective against hygienic pests
and household nuisance pests.

Specific examples of insect pests and acarine
pests to which the method of the present invention can be
applied are given below.

20 Lepidoptera

Plodia interpunctella (Indian meal moth), etc.

Diptera

Culex spp. (common mosquitoes), Anopheles spp.
(Anopheline mosquitoes), Aedes spp., Muscidae (house
25 flies), Drosophilidae (wine flies), Psychodidae (moth
flies), Chironomidae (chironomid midges), Calliphoridae
(blow flies), Sarcophagidae (flesh flies), Simuliidae
(black flies), Tabanidae (tabanid flies), Stomoxiyidae

1 (stable flies), etc.

Coleoptera

Sitophilus zeamais (maize weevil),

Callosobruchus chinensis (adzuki bean weevil), Tribolium

5 castaneum (red flour beetle), Anobiidae (deathwatch and
drugstore beetles), Lyctidae (powder post beetles),
Paederus fuscipes (robe beetle) etc.

Dictyoptera

Blattella germanica (German cockroach),

10 Periplaneta fuliginosa (smokybrown cockroach), Periplaneta
americana (American cockroach), Periplaneta brunnea (brown
cockroach), Blatta orientalis (oriental cockroach), etc.

Hymenoptera

Formicidae (ants), Bethylidae (bethylid wasps),

15 etc.

Siphonaptera

Pulex irritans, etc.

Anoplura

Pediculus humanus capitis (body louse), Pthirus

20 pubis (crab louse), etc.

Isoptera

Reticulitermes speratus, Coptotermes formosanus

(Formosan subterranean termite), etc.

Acarina

25 Mites associated with house dust and stored
food, such as Acaridae, Pyroglyphidae, Cheyletidae, and
the like, Ixodidae such as Boophilus microplus, and the
like, Dermanyssidae, etc.

1 For controlling insects and/or acarines by
vaporizing Compound I, a carrier is not always necessary.
Usually, Compound I is used after being supported on a
suitable carrier.

5 Specific examples of the carriers for adsorption
of Compound I are papers such as filter paper, cardboard
and the like; pulp; plastic resins such as polyethylene,
polypropylene, vinyl chloride and the like; ceramics;
asbestos; glass fiber; carbon fiber; chemical fibers;
10 natural fibers; nonwoven fabrics; substrates for fumigating
mat (a plate formed of fibril of a mixture of cotton linter
and pulp); porous polymer films; porous glass materials;
metal plates (e.g. aluminum dish); etc. These carriers
which have Compound I supported thereon can be used in any
15 preparation form. In the case plastic resins are used as a
carrier, the plasticity of the preparation can be improved
by blending therein a plasticizer such as dioctylphthalate.

 However, a carrier is not always necessary.

When there is any article made of the above material in a
20 room in which insects or acarines, or both, are to be
controlled, it is sufficient that Compound I is supported
on the article.

The vaporizing efficiency can be further
increased by adding subliming materials such as
25 adamantan, cyclododecane, trimethylnorbornane, etc., as
adjuvant for promoting the vaporization.

It is also possible to enhance the efficacy by
using Compound I in admixture with known synergists

1 effective for allethrin and pyrethrins, etc., specific
examples of which being synergists for pyrethroid such as
α-[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-
propyltoluene (piperonyl butoxide), N-(2-ethylhexyl)-
5 bicyclo[2,2,1]hepta-5-ene-2,3-dicarboxyimide (MGK-264^(R)),
octachlorodiisopropyl ether (S-421^(R)), Synepirin-500^(R),
etc.

The activity of Compound I can be stabilized by
using Compound I as a blend with an antioxidant and an
10 ultraviolet absorber for increasing the stability to
light, heat, oxidation, etc. Specific examples of the
antioxidant are 2,2'-methylenebis(6-tert-butyl-4-
ethylphenol), 2,6-di-tert-butyl-4-methylphenol (BHT),
2,6-di-tert-butylphenol, 2,2'-methylenebis(6-tert-butyl-
15 4-methylphenol), 4,4'-methylenebis(2,6-di-tert-
butylphenol), 4,4'-butyldenebis(6-tert-butyl-3-
methylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol),
and dibutylhydroquinone (DBH). The specific examples of
the ultraviolet absorber are phenol derivatives such as
20 BHT, bisphenol derivatives, arylamines such as
condensation products between phenyl- α -naphthylamine,
phenyl- β -naphthylamine or phenetidine and acetone, and
benzophenone compounds.

Compound I may be used in admixture with dyes
25 such as allylaminoanthraquinone, 1,4-diisopropylamino-
anthraquinone, 1,4-diaminoanthraquinone, 1,4-dibutyl-
aminoanthraquinone, 1-amino-4-anilinoanthraquinone and the
like, and perfumes for vaporizable composition.

1 In supporting Compound I on a carrier, there
can, if necessary, be used additives such as fatty acid
esters (e.g. isopropyl myristate, isopropyl palmitate and
hexyl laurate) and organic solvents (e.g. isopropyl
5 alcohol, polyethylene glycol and deodorized kerosine) in
order to lower the viscosity and facilitate impregnation.

The carrier having Compound I supported thereon
which is obtained in the manner described above can be
used as it is by allowing Compound I to vaporize without heating.

10 It exhibits a high insecticidal and/or acaricidal activity
when placed not only in a narrow space but also in a wider
space such as a room, storage chamber, closet, warehouse,
vehicle, ship, airplane, store, cattle shed, stable,
drainage trench, sewer, etc.

15 In the method of the present invention, the
application rate of Compound I is not critical. It should
be determined in view of many factors such as the
concentration of Compound I, type of formulations, manner
and timing of application, environmental temperature and
20 humidity, space to be applied and the width thereof,
whether the space is open or not, whether natural or
artificial air streams go through the space or not, kind
of insects or acarines to be controlled, habitat of
insects or acarines, etc. However, Compound I is usually
25 applied in a ratio of from 1 mg/m³ to 500 g/m³,
preferably 10 mg/m³ to 5 g/m³. This is only a rough
standard and Compound I may be applied beyond the range as
occasion demands.

1 Forming an air stream by stirring the air by
artificial wind from a motorized fan (e.g. an electric
fan) or from an air-conditioner or by natural wind may
encourage the insecticidal and/or acaricidal efficacy of
5 the method of the present invention so as to enable to
apply the method in a wider space.

Compound I can be prepared according to the process disclosed in JP-B-55-42045, for example.

Compound I has optical isomers due to the
10 asymmetric carbon atoms in the alcohol moiety and the acid
moiety. It also has geometrical isomers due to the
cyclopropane ring in the acid moiety. Some of them are
shown in Table 1. Of the isomers, Compounds [I]-A, [I]-B
and [I]-C are more active than the other isomers.

Table 1

Symbol of compound	Configuration of the alcohol moiety	Configuration of the acid moiety
[I]-A	S	1R-trans
[I]-B	S	1RS-trans
[I]-C	RS	1R-trans
[I]-D	RS	1RS-cis
[I]-E	RS	1RS-cis, trans

1 The following reference example, formulation
examples and test examples serve to give specific
illustration of the present invention but they are not
intended in any way to limit the scope of the present
5 invention.

Reference Example

Compound [I]-A was prepared as follows:

0.50 Grams of (1S)-1-ethynyl-2-methyl-2-pentenol
(described in JP-B-63-52615) was dissolved in dry toluene,
10 and 0.50 g of pyridine was added thereto. To the
resulting solution was added 0.90 g of (1R)-trans-3-(2,2-
dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid
chloride (the corresponding carboxylic acid is described
in JP-A-62-253398, for example). The resulting solution
15 was stirred overnight at room temperature. The reaction
mixture, after water had been added thereto, was extracted
with toluene. The organic layer was washed successively
with dilute aqueous hydrochloric acid, saturated aqueous
solution of sodium hydrogen carbonate and saturated
20 aqueous solution of sodium chloride. Thereafter, the
layer was dried over anhydrous sodium sulfate. The dried
layer was filtered and concentrated to obtain a residue.
Purifying the residue with silica gel chromatography
(eluent: a 10:1 mixture of hexane and ethyl acetate) gave
25 1.05 g of (1S)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-
(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
(Compound [I]-A) in a yield of 83%.

1 $n_D^{20.5}$: 1.5063

5 $[\alpha]_D^{24}$: -7.2° (dimethyl ether, C=0.53)

Formulation Example 1

In an adequate amount of acetone was dissolved
5 100 mg of Compound I. The solution was uniformly coated
on a filter paper having an area of 10 cm square and a
thickness of 0.3 cm. Air-drying the paper to remove
acetone therefrom gave a composition capable of vaporizing
the active ingredient without heating (hereinafter a
10 non-heating type vaporizable preparation).

Formulation Example 2

In an adequate amount of acetone were dissolved
200 mg of Compound I and 100 mg of BHT. The solution was
uniformly coated on a filter paper having an area of 10 cm
15 x 15 cm and a thickness of 0.3 cm. Air-drying the paper
to remove acetone therefrom gave a non-heating type
vaporizable preparation.

Formulation Example 3

In an adequate amount of acetone was dissolved
20 600 mg of Compound I, and a 10 cm x 15 cm filter paper was
allowed to absorb the resulting solution uniformly.
Air-drying the paper to remove acetone therefrom gave a
non-heating type vaporizable preparation.

1 Formulation Example 4

In an adequate amount of acetone was dissolved 200 mg of Compound I. The solution was poured into an aluminum dish having an inner diameter of 9 cm so that the 5 solution was spread uniformly in the bottom. Air-drying the dish to remove acetone therefrom gave a non-heating type vaporizable preparation.

Formulation Example 5

250 Milligrams of Compound I and 250 mg of 10 polyethylene glycol were dissolved in an adequate amount of acetone. With the mixture was uniformly impregnated a substrate for fumigating mat (a plate formed of fibril of a mixture of cotton linter and pulp) having a size of 10 cm x 30 cm and a thickness of 0.28 cm. Air drying the 15 mat to remove acetone therefrom gave a non-heating type vaporizable preparation.

Formulation Example 6

65 Parts by weight of powdery polyvinyl chloride are admixed with 30 parts by weight of dioctylphthalate as 20 a plasticizer. The mixture is heat-melted at 150°C. To this thermoplastic resin is blended 5 parts by weight of Compound I, and the resulting mixture is well kneaded in a closed system. The kneaded mixture is injection-molded into a plate having a size of 5 cm x 6.5 cm and a 25 thickness of 0.5 cm and cooled to obtain a non-heating type vaporizable preparation.

1 In the following test examples, the members
tested of Compound I are indicated by the symbols shown in
Table 1, and the compounds used for comparison are
indicated by the symbols shown in Table 2.

Table 2

Symbol of compound	Chemical name	Remarks
(A)	(RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1R)-trans-chrysanthemate	bioallethrin
(B)	(RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-cis,trans-chrysanthemate	empenthrin
(C)	2,2-Dichlorovinyl dimethylphosphate	dichlorvos

5 Test Example 1

The following test was carried out using an aluminum dish obtained according to Formulation Example 4. The amount of active ingredient was adjusted to 0.005 mg/aluminum dish.

10 Twenty female adult houseflies (Musca Domestica, CSMA-strain) were released in a polyethylene cup (diameter: 9 cm, height: 4.5 cm). Then, the upper part of the cup was covered with a 16-mesh nylon net. The cup was closed with the aforesaid aluminum dish so that the
15 agent-treated surface of the dish might face the inside of

- 1 the cup. The nylon net was for preventing direct contact
of the insects with the agent-adhered surface. After the
lapse of 120 minutes at 27°C, the aluminum dish was
removed and water and diet were given to the insects.
- 5 After 24 hours, the dead and alive were counted for
mortality (two replications).

Table 3 shows the results.

Table 3

Compound tested	Mortality (%)
[I]-A	100
[I]-B	100
[I]-C	100
(A)	0
(B)	2.5
(C)	5
Untreated	2.5

Test Example 2

- A filter paper preparation obtained according to
10 Formulation Example 1 except for changing the amount of
the active ingredient to 3.4 mg/filter paper, was
suspended in a glass chamber of 0.34 m^3 (70 cm cube) in
midair with a string having a length of 10 cm from the
center of the ceiling of the glass chamber. The amount
15 used of the active ingredient per unit space was 10

1 mg/m³. The room temperature was 25°C.

After the lapse of 30 minutes, 20 female adult common mosquitoes (Culex pipiens pallens) were released in the chamber. 60 Minutes after releasing the insects, the 5 knocked-down insects were counted for percentage of knocked-down insects. (two replications).

Table 4 shows the results.

Table 4

Compound tested	Knocked-down (%)
[I]-A	100
[I]-B	100
[I]-C	100
(A)	0
(B)	55
(C)	65
Untreated	0

Test Example 3

A filter paper preparation obtained according to 10 Formulation Example 3 was cut up into six equal pieces having a size of 5 cm x 5 cm (amount of active ingredient: 100 mg/piece of filter paper).

Twenty adults of Tyrophagus putrescentiae were placed in a glass Petri dish having a diameter of 9 cm and 15 a height of 2 cm together with diet. Then the mouth of

1 the Petri dish was covered with a 16-mesh nylon net. The
aforesaid filter paper piece was placed on the nylon net,
and the Petri dish was closed with another Petri dish
having the same size. The assembly thus obtained was
5 allowed to stand at room temperature (30°C) and at a
humidity of 75%. After 24 hours, the dead and alive were
counted for mortality. (two replications).

Table 5 shows the results.

Table 5

Compound tested	Mortality (%)
[I]-A	100
[I]-B	100
[I]-C	100
Untreated	7.5

Test Example 4

10 Residual activity test was carried out as follows with a substrate for fumigating mat prepared according to Formulation Example 5 (the amount of active ingredient: 250 mg/mat).

In a Peet Grady's chamber of 6.1 m^3 (183 cm³ cube), the mat was suspended in midair with a string having a length of 20 cm from the center of the ceiling. Then, the mat was left suspended for 9 hours at room temperature (25°C). The amount used of active ingredient

1 per unit space was 41 mg/m³. Nine hours later, 100 adult houseflies (Musca domestica) were released in the chamber. The number of houseflies knocked down in 30 minutes was counted for percentage of knocked down insects.

5 After the test, the mat was taken from the chamber. It was suspended with a cord in midair in a corrugated cardboard box (size: 30 cm x 28 cm, height: 36 cm). The box was allowed to stand in a room at 25°C.

The same test was repeated with the mat stored
10 in the corrugated cardboard box for 1, 3, 5, 8 and 12 weeks after the initial test. Table 6 shows the results.

Table 6

Compound tested	Knocked-down (%)				
	Initial	After 1 week	After 3 weeks	After 5 weeks	After 8 weeks
[II]-A	100	100	100	100	100
(A)	0	3	1	3	2
(B)	100	100	100	80	42
(C)	100	100	76	44	1.9
Untreated	0	2	1	3	0

WHAT IS CLAIMED IS:

1. A method for controlling insects and/or acarines comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate without heating the same.
2. A method for controlling insects and/or acarines comprising vaporizing 1-ethynyl-2-methyl-2-pentenyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.
3. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate without heating the same.
4. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.
5. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1RS)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate without heating the same.
6. A method for controlling insects and/or acarines comprising vaporizing (1S)-1-ethynyl-2-methyl-2-pentenyl (1RS)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate at 0° to 30°C.
7. A method for controlling insects and/or acarines comprising vaporizing (1RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclo-

propanecarboxylate without heating the same.

8. A method for controlling insects and/or acarines comprising vaporizing (1RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclo-propanecarboxylate at 0° to 30°C.

9. A method according to any preceding claim substantially as herein described and exemplified.